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METHODS AND COMPOSITIONS FOR OPTIMIZING INTERFACIAL
PROPERTIES OF MAGNETORESISTIVE SENSORS

Field of the Invention

This invention relates to methods and compositions for optimizing the interfacial properties of magnetoresistive sensors, and specifically data storage devices such as spin valve sensors and giant magnetoresistive (GMR) sensors.

Description of the Prior Art

Significant progress has occurred over the past two decades in the design of multilayered nanostructured thin film systems. Large GMR current-in-plane (CIP) effects have been described in a Fe/Cr multilayered system, approximating a magnetoresistance effect ($\Delta R/R$) of 100 percent, which is a change by a factor of two in resistance with an adequate external field. Since then, many other multilayer GMR and spin valve sensors have been explored. To date, the highest GMR effect is in the Fe/Cr system and is approximately 150 percent at a measurement temperature of 5°K, and remains the largest value observed at any temperature to date. Both the GMR and spin valve effects are characterized by $\Delta R/R$, which is defined as the change in resistance divided by the initial resistance, and is $(R_0 - R_H)/R_0$, where R_0 is the sensor resistance without an external magnetic field and a R_H is the resistance at a minimum external field required to maximize $\Delta R/R$.

Numerous theoretical studies have attempted to explain the behavior of spin valve and GMR effects. However, there does not currently exist an explanation of the main factors controlling

1 the magnitude of the sensor response, as characterized by $\Delta R/R$,
2 as it relates to the required properties of the conductive
3 spacers and ferromagnetic (FM) layers constituting such device.
4 Experimental efforts have been largely based on trial and error,
5 by investigating with various combinations of FM layers and
6 conductive spacer layers. None of the previous work has yielded
7 quantitative guidelines for the maximization of $\Delta R/R$ for spin
8 valve or GMR sensors by providing selection criteria for the
9 layer compositions of the FM material and the conductive spacer.

10
11 Summary of the Invention

12 An object of this invention is to provide means and methods for
13 optimizing the manufacturing process of various magnetoresistive
14 devices, including but not limited to thin film devices such as
15 sensors used in data storage devices.

16
17 Another object of this invention is to provide guidelines for
18 optimizing the selection of multilayer compositions by matching
19 or minimizing the difference in the electronegativities (χ) of
20 adjacent ferromagnetic layers and conductive spacers.

21
22 Still another object of the present invention is to maximize the
23 signal output, as represented by $\Delta R/R$ of spin valve sensors and
24 GMR sensors.

25
26 A further object of this invention is to maximize the thermal
27 stability of spin valve sensors and GMR sensors.

28
29 Yet another object of this invention is to maximize the corrosion
30 resistance of spin valve sensors and GMR sensors.

1
2 Another object of the invention is to provide conductive spacers
3 which minimize electromigration in the FM and spacer layers,
4 which extend the useful lifetimes of spin valve and GMR sensors.

5
6 Another object is to provide for multiple interfacial matching of
7 an FM layer with its contacting conductive spacers.

8 In accordance with this invention, spin valve sensors and GMR
9 sensors are made with layers of FM material and conductive
10 spacers interposed between the FM layers. The difference in
11 electronegativities between the layers and spacers is minimized.

12 A relatively low resistivity and/or a large mean free path is
13 provided by the conductive spacer material. As a result of these
14 conditions, the $\Delta R/R$ of the sensor is maximized. The novel
15 sensor is also corrosion resistant, exhibits greater chemical and
16 thermal stability, and signal output of the sensor device is
17 increased.

18
19 A method for optimizing the interfacial properties of a
20 magnetoresistive sensor, such as a GMR or spin valve, is
21 disclosed. The method includes selecting one or more FM layers
22 having at least a first electronegativity, and selecting one or
23 more conductive spacers having at least a second
24 electronegativity, such that the selecting steps include the step
25 of substantially matching or minimizing the difference between
26 the first and second electronegativities and thereby minimizing
27 the difference between the electronegativities of the selected
28 spacers and FM layers.

29
30 Brief Description of the Drawing

1 The invention will be described in greater detail with reference
2 to the drawings in which:

3
4 Fig. 1 is a cross-sectional view depicting a spin valve sensor
5 made in accordance with this invention;

6
7 Fig. 2 is a cross-sectional view depicting a GMR sensor made in
8 accordance with this invention;

9
10 Fig. 3 is a graph plotting a relationship between a square root
11 of the absolute value of an electronegativity difference (i.e.,
12 $|\Delta\chi|^{1/2}$) versus $\Delta R/R$ for spin valve sensors with various
13 ferromagnetic/conductive spacer interfaces;

14
15 Fig 4 illustrates three curves plotting the relationship between
16 $|\Delta\chi|^{1/2}$ versus $\Delta R/R$ for various spin valve sensors at different
17 temperatures;

18
19 Fig. 5 illustrates three curves plotting the relationship between
20 $|\Delta\chi|^{1/2}$ versus $\Delta R/R$ for various GMR sensors illustrating the
21 first, second and third peaks of GMR response;

22
23 Fig. 6 illustrates a curve plotting the relationship between
24 $|\Delta\chi|^{1/2}$ versus $\Delta R/R$ for various GMR sensors having various crystal
25 structures.

26
27 Fig. 7 is a chart that illustrates various exemplary combinations
28 and compositions of FM layers and spacers for use in spin valve
29 and GMR sensors;

1 Fig. 8 illustrates two curves plotting the electrical resistivity
2 in microohm-cm versus the atomic composition for a Cu-Au alloy
3 system;

4
5 Fig. 9 illustrates two graphs plotting the electrical resistivity
6 in microohm-cm versus the atomic composition for a CuPt alloy
7 system;

8
9 Fig. 10 illustrates a use of random crystal orientation in a spin
10 valve sensor made according to the present invention;

11
12 Fig. 11 illustrates a use of preferred crystal orientation in a
13 spin valve sensor made according to the present invention;

14
15 Fig. 12 is a cross-sectional view of a spin valve sensor with
16 compound interfaces made according to the present invention; and

17
18 Fig. 13 is a cross-sectional view of a giant magnetoresistive
19 sensor with compound interfaces made according to the present
20 invention.

21
22 Similar numerals refer to similar elements in the drawings. It
23 should be understood that the sizes of the different components
24 in the figures are not necessarily in exact proportion, and are
25 shown for visual clarity and for the purpose of explanation.

26
27 Detailed Description of the Invention

28 Fig. 1 is a partial cross-section representing a spin valve
29 magnetoresistive (MR) sensor 10 made according to the present
30 invention. The spin valve sensor 10 is formed of two FM layers

1 (i.e., FM1 and FM2), that are separated by a conductive spacer or
2 layer 12. The sensor 10 is formed on a nonmagnetic substrate on
3 which a buffer layer, about 25-100 Angstroms (\AA) thick, is
4 deposited. The buffer layer is made from Ta, Cr, Fe, Pt, Pd, Ir
5 or Au. The FM layers FM1 and FM2 may have the same or different
6 composition. If the difference in coercivity between FM1 and FM2
7 is sufficient (e.g., approximately 50 to 100 Oersteds), a
8 magnetoresistance effect will be observed when an external field
9 changes from positive to negative and a magnetic configuration of
10 one of the layers changes while the other remains stationary.
11 Alternatively, (as shown in Fig.1), the magnetization of one of
12 the FM layers, (e.g., FM2), may be pinned by placing it in atomic
13 contact with an antiferromagnetic (AFM) layer 14, such as an FeMn
14 layer. The magnetization of the unpinned FM layer FM1 is free to
15 rotate in the presence of an external magnetic field.

16
17 The application of an external magnetic field causes a variation
18 in the magnetization orientation of the FM layer FM1, which
19 causes a change in the spin-dependent scattering of conduction
20 electrons and thus in the electrical resistance of the spin valve
21 sensor 10. The resistance of the spin valve sensor 10 changes as
22 the relative alignment of the magnetization of the FM1 layer
23 changes. The FM2 layer remains constrained and its magnetization
24 direction remains the same.

25
26 The present invention includes an empirical relationship between
27 $\Delta R/R$ and the electronegativity difference between adjacent FM
28 layers and conductive spacer layers in spin valve and GMR
29 sensors. This relationship applies to both spin valve and GMR
30 sensors, and shows that $\Delta R/R$ response is a function of the

1 electronegativity mismatch between adjacent FM layers and
2 conductive spacers. It is believed that the mismatch in
3 electronegativities results in a potential barrier at the
4 interface that is related to the absolute value of the difference
5 in the electronegativities of the FM layers and the conductive
6 spacers, i.e., $|\Delta\chi|$. With increasing $\Delta\chi$ mismatch, the $\Delta R/R$
7 amplitude of the spin valve and GMR sensors will decrease to a
8 point where $\Delta R/R$ will approach an intercept value of zero. As
9 shown later, this intercept value uniformly occurs at a value of
10 $|\Delta\chi|^{1/2}$ approximately equal to 0.5 for both spin valve and GMR
11 sensors indicating that the underlying mechanism for obtaining
12 $\Delta R/R$ is the same for both types of sensors.

13
14 Thus, according to a preferred embodiment, the spin valve sensor
15 10 (Fig. 1) is formed by selecting the desired spacer material.
16 Subsequently, the FM layers FM1 and FM2 are selected such that
17 their average electronegativities match or substantially
18 approximate the average electronegativity of the selected spacer
19 12.

20
21 Another condition of the empirical relation relates to the
22 crystal structures of the FM and spacer layers. The FM and
23 spacer layers preferably should have the same or similar crystal
24 structure, e.g., a face-centered cubic ("FCC") FM layer adjacent
25 to an FCC conductive spacer layer or a body-centered cubic
26 ("BCC") FM layer adjacent to a BCC spacer layer. These
27 combinations are referred to herein as "FCC Systems" and "BCC
28 Systems", respectively.
29

1 The lowest $|\Delta\chi|$ reported in an FCC System is in the range of
2 approximately .12 eV. For example, a GMR device comprising
3 70Co:30Fe FM layers and Ag spacers exhibited a $\Delta R/R$ of
4 approximately 100 with a $|\Delta\chi|$ of approximately .12 eV. The
5 lowest $|\Delta\chi|$ reported in a BCC System is in the range of
6 approximately .07 eV. For example, in the GMR device described
7 previously (i.e., Fe/Cr) having a $\Delta R/R$ of approximately 150, had
8 a $|\Delta\chi|$ of approximately .07 eV. Magnetoresistive sensors
9 according to the invention can achieve lower $|\Delta\chi|$ values and,
10 consequently, higher $\Delta R/R$ sensor outputs than previously
11 reported values.

12
13 Fig. 2 illustrates the use of the present inventive concept in a
14 GMR sensor 20. The GMR sensor 20 is a sandwich structure formed
15 of a plurality of layers, such as FM materials, that are
16 separated by a plurality of conductive spacers 22. Although not
17 shown in Fig. 2, the FM/spacer structure can have a multiplicity
18 of repeat units of FM/spacer. In the GMR sensor 20 the
19 electronegativities of each of the successive layers FM are
20 substantially matched or their difference in χ is minimized with
21 respect to the electronegativity of the contiguous spacers 22.

22
23 Fig. 3 illustrates that the linear relationship of the invention
24 is generally maintained irrespective of the composition of the FM
25 and spacer materials. Further, Fig. 4 illustrates that the
26 linear relationship is maintained over a wide range of
27 measurement temperatures. Fig. 5 illustrates that linear
28 relationship holds for a variety of FM alloy compositions for a
29 fixed spacer element. Further, Fig. 6 illustrates that the
30 linear relationship holds for both FCC Systems and BCC Systems.

The percent ionic content of an interface A/B between an FM layer A and a conductive spacer B can be estimated by the electronegativity difference between the FM A and the spacer B as shown in the following equation (Pauling, "The Nature of the Chemical Bond", 98 (1060, 3d)):

$$\text{Percent Ionic Content} = (1 - e^{(\chi_A - \chi_B)^2/4}) \times 100$$

By applying the foregoing empirical finding that $|\Delta\chi|^{1/2} \cong 0.5$ when $\Delta R/R$ approaches zero, it is possible to estimate the percent ionic content of the interface A-B. Specifically, when $|\chi_A - \chi_B|^{1/2} = |\Delta\chi|^{1/2} = 0.5$, the ionic content at the interface A-B is approximately 1.5 percent.

Additionally, at the intercept point where $\Delta R/R$ approaches zero, the excess ionic energy at the FM/spacer interface can be estimated to be 1.96 Kcal or 0.085 eV (Pauling, Table 3-6 at page 90). This energy term relates to the electron transmission at the interface, which influences $\Delta R/R$. Thus, at $|\Delta\chi|^{1/2}$ equal to 0.5 electron volts, the probability of electron transmission through a potential barrier at the interface is approximately 0 percent.

By an appropriate selective matching of the electronegativities of the spacer 12 (Fig. 1) and the adjacent FM layers FM1 and FM2, it is possible to maximize the magnetoresistive response (as characterized by $\Delta R/R$), and thus the signal output of the spin valve sensor 10 is maximized.

1 It is also preferable that the bulk resistivities of the
 2 materials used in the FM layers and conductive spacers be
 3 relatively low to ensure a high $\Delta R/R$ sensor output. For
 4 example, in both GMR and spin valve sensors it is desirable that
 5 the bulk resistivities of the FM layer material be less than 100
 6 microohm ($\mu\Omega$) cm, and the spacer material be less than 30 $\mu\Omega$ -cm.

7
 8 Another aspect of the invention is the relationship illustrated
 9 by the following equations:

10
 11 (1a) $|\Delta\chi| = \chi \text{ (FM)} - \chi \text{ (spacer)},$

12 (1b) where: $\chi \text{ (spacer)} = 0.44 \phi \text{ (spacer)} - 0.15,$ and

13 (1c) $\chi \text{ (FM)} = 0.44 \phi \text{ (FM)} - 0.15,$

14
 15 where $\chi \text{ (FM)}$ represents the electronegativity of the FM layers;
 16 $\chi \text{ (spacer)}$ represents the electronegativity of the spacer 12; and
 17 where $\phi \text{ (spacer)}$ and $\phi \text{ (FM)}$ are the work functions of the spacer 12
 18 and FM layers, respectively, as stated in Lange, "Handbook of
 19 Chemistry", 3-9 (1973, 11d). Both χ and ϕ values are expressed
 20 in electron volts (eV.).

21
 22 Each chemical element has a work function ϕ from which the χ of
 23 that element is computed by equations (1b) or (1c). For alloys
 24 or compounds containing additional elements that constitute
 25 either the FM material or the conductive spacer used in the GMR
 26 or spin valve sensors, the χ of such mixtures has been found to
 27 be an additive property of the constituents of the alloy. The χ
 28 of the mixture is the sum of the products of the atomic fraction
 29 of any element in the mixture times the electronegativity of that

1 element summed over all elements constituting the mixture, as
2 illustrated in the following equation:

3
4
$$(2) \quad \chi_{(a-b-c)} = f_a \chi_a + f_b \chi_b + f_c \chi_c,$$

5
6 where f_a , f_b , and f_c refer to the atomic fractions of elements a,
7 b and c, respectively forming the alloy; and χ_a , χ_b and χ_c refer
8 to the electronegativities of elements a, b and c, constituting
9 the alloy. While only a ternary alloy has been considered for
10 illustration purpose, it should be understood that the form of
11 equation (2) is applicable to alloys with any number of elements.
12 In addition, equation (2) applies both to ferromagnets and
13 conductors.

14
15 Prior art methods for fabricating spin valve and GMR sensors
16 included combining spacers made of an electrically conductive
17 elements such as Au, Ag or Cu, with layers of FM materials such
18 as FeCo, NiFe, or elements such as Fe, Co and Ni, without regard
19 to the electronegativity matching between the successive FM
20 layers and conductive spacers. These prior art methods are mainly
21 based on trial and error studies.

22
23 The following Tables I and II provide listings of some exemplary
24 conductors and ferromagnets, (i.e., FCC Systems and BCC Systems),
25 respectively, that can be used to fabricate various devices,
26 including but not limited to magnetoresistive sensors according
27 to the invention.

28
29 The values for χ in Tables I and II were derived from electron
30 work function data (as reported in Michaelson, "The Work Function
31 of the Elements and Its Periodicity," Journal of Applied Physics,

vol. 48, No. 11, November 1977, p. 4729) and equations (1)(b) and (c). Generally, the work functions for randomly oriented crystal structures were used, but if data was provided by Michaelson for specific crystal faces or phases, such work function values were averaged to calculate an average work function, which was used to calculate the following χ values. Further, if the work function for randomly oriented crystals was in the range of such average work function value (i.e., within five percent), the randomly oriented value was added to the previously described work function values and used to compute a second average work function value, which was then used to compute the χ values below. For alloys or compounds, equation (2) was used to compute the χ values below.

TABLE I - FCC SYSTEMS

CONDUCTORS	χ (eV.)	FERROMAGNETS	χ (eV.)
Cu	1.91	80Ni:20Fe	2.084
Ag	1.89	Ni ₃ Fe ⁽⁴⁾	2.07
Ag ₃ Pt ⁽⁵⁾	2.00	Au	2.22-2.27 ⁽³⁾
Ni ₃ Mn ⁽⁴⁾	2.02	Fe ₄ N	2.12
Pt	2.34	FePd	2.11
Pd	2.32	Fe _{1-y} Au _y ⁽¹⁾	$2.0 \leq \chi \leq 2.13$
Cu ₃ Pt ⁽⁴⁾	2.02	Co _{1-z} Au _z ⁽²⁾	$2.07 \leq \chi \leq 2.14$
CuPt ⁽⁴⁾	2.13	Fe _{0.485} Ni _{0.418} Mn _{0.097}	1.99
CuPt ₃ ⁽⁴⁾⁽⁵⁾	2.23	80Ni:20Fe	2.084
Cu ₃ Pt ₅ ⁽⁴⁾⁽⁵⁾	2.18	81Ni:19Fe	2.086
Cu ₃ Au ⁽⁴⁾	1.99-2.00 ⁽³⁾	90Co:10Fe	2.04
Cu ₃ Pd ⁽⁴⁾⁽⁵⁾	2.01	80Ni:20Fe	2.084
CuPd ⁽⁴⁾	2.06		

1 Rh 2.04
 2 CuAu^{(4) (5)} 2.07-2.09⁽³⁾

3
 4 ⁽¹⁾ Where y is an atomic fraction with a value between 0.30 and
 5 0.70;

6 ⁽²⁾ where z is an atomic fraction with a value between 0.10 and
 7 0.50;

8 ⁽³⁾ the higher stated values for χ reflect the use of a larger
 9 work function for the <111> face of Au than that stated in
 10 Michaelson, which adjustment appears necessary when work function
 11 data for <111> faces of other FCC elements is compared to <110>
 12 work function data; and

13 ^{(4) (5)} a pseudo-cubic structure, the stated composition is a
 14 superlattice structure.

15
 16 As noted, some of the compounds in Table I are pseudo-cubic, but
 17 have lattice parameters close to FCC and provide a structure
 18 match adequate for an FCC System.

19
 20 TABLE II - BCC SYSTEMS

21 CONDUCTORS	χ	22 FERROMAGNETS	χ
23 Cr	1.83	24 Fe _{1-u} Cr _u ⁽¹⁾	1.85 ≤ χ ≤ 1.88
25 Cr	1.83	26 Fe _{1-w} V _w ⁽²⁾	1.85 ≤ χ ≤ 1.87
27 Cr	1.83	28 Ternary FeCrV alloys	1.84 ≤ χ ≤ 1.87
29 Cr	1.83	30 Fe ₃ Al ⁽³⁾	1.86
AlFe ₂	1.84		

31 ⁽¹⁾ Where u is an atomic fraction with a value between 0.40 and
 32 0.70;

(²) where w is an atomic fraction with a value between 0.25 and 0.35; and

(³) the stated composition is a superlattice structure.

The following examples are provided for the purpose of illustration and explanation only. They are not intended to be exclusive or to limit the coverage of the present inventive concepts, including the selection process and the sensors. All compositions in the following examples are given in atomic percentage:

Example 1

In Table I above, the electronegativities of the conductors and the ferromagnets represent the atomic fraction weighted electronegativities, as illustrated by the following example for Cu₃Pt:

$$\chi(\text{Cu}_3\text{Pt}) = 0.75\chi(\text{Cu}) + 0.25\chi(\text{Pt}) = 2.02,$$

where $\chi(\text{Cu}_3\text{Pt})$ is the electronegativity of Cu₃Pt; $\chi(\text{Cu}) = 1.91$; and $\chi(\text{Pt}) = 2.34$. This example illustrates that the atomic fraction of the electronegativities of the elements of any alloy conductor or ferromagnet formed of any number of elements, i.e., ternary, quaternary, etc., can be used to calculate the electronegativity of the alloy.

By using Table I above, it is possible to closely match the electronegativities of the conductors and the ferromagnets. For example, having selected Cu₃Pt as the conductor of choice, it would be desirable to select a FM material having a close electronegativity. Table I indicates that one of the closest

1 materials whose electronegativity matches that of Cu_3Pt is Ni_3Mn ,
2 since the average electronegativity of Ni_3Mn is 2.01 and $\Delta\chi$ of
3 the combination is approximately $|0.01|$.
4

5 Example 2

6 Another aspect of the invention concerns the use of materials
7 exhibiting superlattice structures for FM layers and spacers in
8 GMR and spin valve sensors. The prior art does not teach or
9 disclose the use of such superlattice structures in MR sensors.
10 Significant advantages in MR device performance can be achieved
11 with such superlattice structures, even without the matching of χ
12 values.

13
14 For example, Ni_3Mn , a ferromagnetic superlattice intermetallic
15 compound having an electronegativity of 2.01, may be matched with
16 Cu_3Pt , as described in Example 1. The matching of two
17 superlattice structures is desirable in that these ordered
18 structures will improve the thermal stability of sensors
19 containing them. It is believed that this is due to the
20 additional external thermal energy that would be required to
21 disorder one or both superlattice structures before the elements
22 contained in the superlattice would be free to diffuse at the
23 interface. This additional energy ranges between 0.1 eV to 0.3
24 eV above the activation energy for diffusion across the interface
25 between the conductor spacer and the FM layer and accordingly
26 leads to greater thermal stability of the device. Greater
27 corrosion resistance would also be achieved for such devices.
28

29 Example 3

30 A subsequent inquiry may then be made as to whether there exists
31 another ferromagnet with other desirable characteristics, such as

1 minimal magnetostriction (λ_s), higher corrosion resistance,
2 and/or lower resistivity than Ni_3Mn . Ni_3Fe , also a superlattice
3 alloy, with an electronegativity of 2.07, may in certain
4 applications present a more desirable match than Ni_3Mn , due to
5 low coercivity (H_c), low λ_s and superior corrosion resistance
6 and may be matched with a CuAu superlattice having an χ of 2.07.

7
8 Example 4

9 This example identifies conductive spacer alloys useful for the
10 matching or minimizing the $\Delta\chi$ values between the spacer alloys
11 and appropriate ferromagnetic elements or alloys thereof.

12
13 In addition to CuAu and CuPt alloys and their superlattice
14 compositions referred to previously, binary, ternary or higher
15 order alloys of elements such as Cu, Ag, Au, Pt, Pd, Ir, Rh and
16 Ru may be used to match appropriate FMs and provide χ values
17 ranging from approximately 1.89 to 2.33. Such alloys may be used
18 to fabricate various devices, including but not limited to spin
19 valve and GMR sensors, based on the electronegativity matching or
20 minimizing of the differences in electronegativities of the
21 present invention. Other superlattice alloys similar to CuPt and
22 CuAu that exhibit ordering phenomena, such as Ag_3Pt and AgPt , may
23 also be used for implementing this invention.

24
25 Example 5

26 A subsequent inquiry may then be made as to whether the
27 crystallographic structures of the adjacent conductive spacer and
28 the FM layer are matched. It is desirable to match the
29 crystallographic structures of adjacent layers. The following is
30 a list of additional intermetallic compounds having a FCC

crystallographic structure for use as conductive spacer materials:

	χ
AgPt ₃	2.23
CrIr ₃	2.20
Cr ₂ Pt	2.00

The following is a list of additional conductive spacer elements having a BCC crystallographic structure:

	χ		χ		χ
Cr	1.83	V	1.74	Mo	1.83
W	1.80	Nb	1.74	Ta	1.67

A number of the above elements such as W, Ta and Mo occur in high resistivity structures when deposited by evaporation or sputtering.

However, by controlling deposition parameters (such as rates, substrate temperatures, and partial inert gas pressures, e.g., Ar), a low resistivity structure can be obtained, which is preferred for spacers in spin valve and GMR structures.

The following is an example confirming the desirability of matching the crystallographic structures of adjacent FM/spacer layers. Even though the electronegativity of Fe (1.90) closely matches the electronegativity of Ag (1.89), the resulting $\Delta R/R$ of the FeAg structure is small because of the Fe and Ag crystal structure dissimilarities and attendant potential barriers accruing therefrom. Specifically, Fe has a BCC structure, while Ag has an FCC structure.

Example 6

The foregoing inventive principles and examples are applicable at room temperature as well as other temperatures, such as cryogenic temperatures, e.g., 5 °K. Fe having a BCC structure and an electronegativity of 1.90, and Cr having a BCC structure as well and an electronegativity of 1.83 results in a very high $\Delta R/R$. This electronegativity mismatch is the smallest one experimentally measured, i.e., 0.07 and results in attainment of the highest observed $\Delta R/R$ (approximately 150 percent) at a 5° Kelvin measurement temperature.

Fig. 3 illustrates the linear relationship between the magnetoresistive response as characterized by $\Delta R/R$ of the spin valve sensor 10 (Fig. 1), relative to a square root of the absolute value of the electronegativity difference, (i.e., $|\Delta\chi|^{\frac{1}{2}}$) of the FM layers FM1, FM2 and the spacer 12, at room temperature, for a coupling field less than or equal to approximately 10 Oersteds. This linear relationship is represented by a curve S1. It is maintained for various spin valve layer compositions, representing a variety of spacer materials and FM materials and illustrates that the variable $\Delta\chi$ controls $\Delta R/R$. This relation may be expressed generally by the following equation (3):

$$(3) \Delta R/R \cong A - B |\Delta\chi|^{\frac{1}{2}},$$

where A and B are constant values.

Sample preparation variables may affect the slope B of this equation (3). It is generally recognized in the literature that a certain degree of roughness at the interface between the FM layers

1 and the conductive spacers produces a maximum result ($\Delta R/R$) for a
2 given interface, for instance, Dieny, "Giant Magnetoresistance in
3 Spin-Valve Multilayers", Journal of Magnetism and Magnetic
4 Materials, 136 (1994) pp. 335-359. As the roughness increases or
5 decreases from its optimal value $\Delta R/R$ will decrease from its
6 optimal value. This will change the slope B, but will not modify
7 the general principles of the invention. Roughness variations will
8 also not modify the intercept where $\Delta R/R$ equals 0, which remains at
9 $|\Delta\chi|^2$ equals 0.5.

10
11 When spin valves and GMR sensors achieve the condition described by
12 $|\Delta\chi|^2$ equal to or greater than 0.5, then $\Delta R/R$ equals 0 and B equals
13 approximately 2A. In this case, equation (3) may be expressed as
14 follows:

15
16
$$(4) \Delta R/R \approx A - 2A |\Delta\chi|^2$$

17

18 In an exemplary embodiment of the spin valve sensor 10, the general
19 equation (3) may be expressed by the following experimentally
20 derived equation (5) for spin valves formed by a variety of
21 interfaces:

22
23
$$(5) \Delta R/R = 32.3 - 64.6 |\Delta\chi|^2.$$

24

25 The following interfaces were used in deriving this equation:
26 Co/Cu/Co, Co/Cu/80Ni:20Fe, 80Ni:20Fe/Cu/80Ni:20Fe, Co/Au/80Ni:20Fe,
27 Ni/Cu/Ni, 80Ni:20Fe/Pt/80Ni:20Fe and 80Ni:20Fe/Pd/80Ni:20Fe. The
28 following experimental examples verify equation (5) above.

29
30 Example 7

1 Point D on curve S1 in Fig. 3 represents the following FM
2 layer/spacer compositions: Co/Cu/Co, where the first element Co is
3 the unpinned FM layer FM1, the second element Cu is the conductive
4 spacer 12 (Fig. 1), and the third element Co is the pinned FM layer
5 FM2. Pursuant to equation (5), the composition of this example
6 yields a $\Delta R/R$ of approximately 9.5 percent.

7
8 Example 8

9 Point E on curve S1 in Fig. 3 represents Co/Cu/80Ni:20Fe, where the
10 first element Co is the unpinned FM layer FM1 (Fig. 1), the second
11 element Cu is the conductive spacer 12, and the third element
12 80Ni:20Fe is the pinned FM layer FM2. Pursuant to equation (5), the
13 composition of this example yields a $\Delta R/R$ of approximately 6.5
14 percent.

15
16 Example 9

17 Point F on curve S1 in Fig. 3 represents 80Ni:20Fe/Cu/80Ni:20Fe,
18 where the first element 80Ni:20Fe is the unpinned FM layer FM1
19 (Fig. 1), the second element Cu is the conductive spacer 12, and
20 the third element 80Ni:20Fe is the pinned FM layer FM2. Pursuant to
21 equation (5), the composition of this example yields a $\Delta R/R$ of
22 approximately 5 percent.

23
24 Example 10

25 Point G on curve S1 in Fig. 3 represents Co/Au/80Ni:20Fe, where
26 the first element Co is the unpinned FM layer FM1 (Fig. 1), the
27 second element Au is the conductive spacer 12, and the third
28 element 80Ni:20Fe is the pinned FM layer FM2. Pursuant to equation
29 (5), the composition of this example yields a $\Delta R/R$ of approximately
30 4.5 percent.

Example 11

Point H on curve S1 in Fig. 3 represents Ni/Cu/Ni, where the first element Ni is the unpinned FM layer FM1 (Fig. 1), the second element Cu is the conductive spacer 12, and the third element Ni is the pinned FM layer FM2. Pursuant to equation (5), the composition of this example yields a $\Delta R/R$ of approximately 2.5 percent.

Example 12

Point I on curve S1 in Fig. 3 represents 80Ni:20Fe/Pt/80Ni:20Fe, where the first alloy 80Ni:20Fe is the unpinned FM layer FM1 (Fig. 1), the second element Pt is the conductive spacer 12, and the third alloy 80Ni:20Fe is the pinned FM layer FM2. Pursuant to equation (5), the composition of this example yields a $\Delta R/R$ of approximately 0.3 percent.

Example 13

Point J on curve S1 in Fig. 3 represents 80Ni:20Fe/Pd/80Ni:20Fe, where the first alloy 80Ni:20Fe is the unpinned FM layer FM1 (Fig. 1), the second element Pd is the conductive spacer 12, and the third alloy 80Ni:20Fe is the pinned FM layer FM2. Pursuant to equation (5), the composition of this example yields a $\Delta R/R$ of approximately 0.2 percent.

The $\Delta\chi$ s in examples 7, 8, 9 and 11 yield positive values, whereas examples 10, 12 and 14 yield negative values of $\Delta\chi$; however, by using the absolute value, i.e., $|\Delta\chi|^{1/2}$, all combinations are predicted by the results of equation 5. This illustrates that the interfacial barrier characteristics are indifferent to the sign of $\Delta\chi$ and only respond to its magnitude.

Example 14

Point K on curve S1 in Fig. 3 represents 80Ni:20Fe/Al/80Ni:20Fe, where the first alloy 80Ni:20Fe is the unpinned FM layer

FM1 (Fig. 1), the second element Al is the conductive spacer 12, and the third alloy 80Ni:20Fe is the pinned FM layer FM2. The square root of the electronegativity difference $|\Delta\chi|^{1/2}$ between Al and its adjacent first alloy layer FM1 is approximately 0.6/eV, which is greater than the intercept point value of 0.5 eV. In this and other similar examples where $|\Delta\chi|^{1/2}$ is greater than 0.5 eV, i.e., greater than the intercept point, then $\Delta R/R$ is set equal to zero. This example illustrates that even when the crystallographic structures of adjacent layers are matched, i.e., both 80Ni:20Fe and Al have FCC structures, the sensor output signal ($\Delta R/R$) may be low because the χ s of the layers are not matched. However, Al may be useful if its χ is matched with that of an appropriate FM material.

While the relationship described in the equations above, i.e., between the sensor output signal ($\Delta R/R$) and the absolute difference in electronegativities of adjacent layers has been described in view of data obtained at room temperature, further analyses confirm that these relationships are also valid for data obtained at other temperatures, including the normal sensor operating temperatures and at cryogenic temperatures as well. It should however be noted that, as shown in Fig. 4, the slope of the curve S1, i.e., the constant value A, will vary at different temperatures.

The relationship between $\Delta R/R$ and $|\Delta\chi|$ as previously expressed has been developed for spacer materials having bulk resistivities

of approximately less than $10 \mu\Omega\text{-cm}$. It is expected that some deviation from the linear relationship between $\Delta R/R$ and $|\Delta\chi|^2$ will occur for larger resistivities in the spacer materials, i.e., a partial loss in the expected value of $\Delta R/R$ with increasing resistivity of the spacer material above the range of approximately $10 \mu\Omega\text{-cm}$.

The following examples 15 through 17 are made with reference to Fig. 4 which illustrates the temperature insensitivity of the linear relationships between the $\Delta R/R$ of the spin valve sensor 10 (Fig. 1) relative to the square root of the absolute value of the electronegativity difference $|\Delta\chi|^2$ of the average electronegativity of the pinned and unpinned FM layers FM1 and FM2 and the spacer 12. The response is shown at three different measurement temperatures, that is, 300°K , 200°K and 100°K .

Example 15

This example is represented by the curve V1 of Fig. 4 and graphically plots the linear relationship of equation (3) at a measurement temperature of 100°K . Points a, b and c reflect data for the following respective spin valve (Fig. 1) combinations:

unpinned FM layer FM1: Co (point a), 80Ni:20Fe (point b), and Ni (point c),
pinned FM layer FM2: (80Ni:20Fe), and
conductive spacer: Cu with an approximate thickness of 22\AA .

The χ values used for the FM layers are the average of pinned and free layers, $(\chi_{\text{free}} + \chi_{\text{pinned}})/2$.

1
2 Example 16

3 This example is represented by the curve V2 and graphically plots
4 the linear relationship at a temperature of 200°K. Points d, e
5 and f reflect data observed for similar compositions as in
6 Example 15 above.
7

8 Example 17

9 This example is represented by the curve V3 and graphically plots
10 the linear relationship at a temperature of 300°K. Points g, h
11 and i reflect data observed for similar compositions as in
12 Examples 15 and 16 above.
13

14 For spin valve structures, the conductive spacer separating the
15 FMs is generally between 18Å° and 30Å° thick, while the FMs
16 generally range between 30Å° and 120Å° with an optimum thickness
17 typically near 60Å° each.
18

19 Prior to the teaching of the relationships of the forms of
20 equations (3) and (4), no known method to maximize $\Delta R/R$ was
21 available in the prior art. By using equations (3) and (4) it is
22 now possible to rationalize the selection of the materials
23 forming the FM layers and the conductive spacers, thus
24 substantially minimizing or eliminating the need for conventional
25 trial and error selection processes. Consequently, the selection
26 process can now be automated and/or rationalized, and significant
27 cost savings can be achieved in the development of superior spin
28 valve and GMR sensors. More particularly, an appropriate
29 selection of materials can significantly improve the signal

output of the spin valve sensor 10 (Fig. 1), which is a result that is highly sought and of great commercial value.

Fig. 5 illustrates that the linear relationship of equation (3) for the GMR sensor 20 (Fig. 2) is exhibited for distinct MR peaks at particular spacer thicknesses. $\Delta R/R$ was measured at room temperature, for various Co Ni alloys. The resulting relationships are represented by three exemplary curves G1, G2, G3, and are for various GMR FM layer compositions. The curves G1, G2, G3 may be expressed generally by the following equations (6), (7) and (8), that continue to verify the relationships of equations (3) and (4).

Curve G1 in Fig. 5 may be expressed by the following equation (6), and represents the GMR first peak at a Cu thickness of approximately 10A°:

$$(6) \quad \Delta R/R \cong 245 - 490 |\Delta\chi|^{\frac{1}{2}}.$$

Curve G2 in Fig. 5 may be expressed by the following equation (7), and relates to the second GMR peak at a Cu thickness of approximately 22A°:

$$(7) \quad \Delta R/R \cong 110 - 220 |\Delta\chi|^{\frac{1}{2}}.$$

Curve G3 in Fig. 5 may be expressed by the following equation (8), and represents the third GMR peak at a Cu thickness of approximately 32A° to 36A°:

$$(8) \quad \Delta R/R \cong 45 - 90 |\Delta\chi|^{\frac{1}{2}}.$$

1
2 While only three GMR peaks are shown in Fig. 5, well defined
3 peaks at a fourth position (i.e., peaks 1 through 4) have been
4 observed in GMR devices. These peaks generally occur at spacer
5 thicknesses of approximately 10\AA , 20\AA , 30\AA and 40\AA . It is
6 known that both the peak $\Delta R/R$ and the switching field required
7 to attain the maximum value of $\Delta R/R$ (at any peak) decline with
8 increasing peak number (and increasing spacer thickness).
9 However, the switching field at each increasing peak declines
10 more rapidly than does $\Delta R/R$ at each peak. Thus, the sensitivity
11 of the transducer as measured by $\Delta R/R/\text{Oersted}$ of switching field
12 improves dramatically with increasing peak number. Consequently,
13 the present invention is particularly useful in extending GMR
14 performance to higher peak values at lower switching fields due
15 to the minimizing of Δx between FM and spacer layers. Thus, the
16 present invention maximizes the device sensitivity at any peak
17 but is most useful at large peak numbers that are inherently more
18 sensitive, i.e., achieving a larger ($\Delta R/R/\text{Oersted}$) than has been
19 reported. Depending on the particular application, it is possible
20 to select any of the GMR peaks. Additionally, in GMR structures
21 the FM layers may range in thickness from approximately 4\AA to
22 25\AA

23
24 By using equations (3) and (6), (7) and (8) it is possible to
25 simplify the selection of the materials forming the various FM
26 layers and conductive spacers 22 of the GMR sensor 20 (Fig. 2),
27 similarly to what has been explained above in relation to the
28 spin valve sensor 10 (Fig. 1). Again, the control of the
29 interfacial roughness at the FM/spacer contact will be required
30 to achieve maximum $\Delta R/R$.

1
2 In addition, the following exemplary embodiments demonstrate that
3 by a proper selection of the composition of the materials forming
4 the sensor 20 (Fig. 2), and by matching or substantially
5 minimizing the absolute electronegativity difference (or
6 mismatch) of the sensor layers (FM layers and conductive
7 spacers), it is possible to obtain significantly higher output
8 signals ($\Delta R/R$) than those previously attained. The foregoing
9 linear relationships were mostly obtained using data at room
10 temperature. Further analyses confirm that these relationships
11 are also valid for data obtained or derived at other
12 temperatures, including the sensor normal operating temperatures
13 of approximately 45°C and cryogenic temperatures as well.
14 However, the slopes of the curve G1, G2 and G3, i.e., the value
15 B, will vary at different temperatures.

16
17
18 An important aspect of the present invention may be derived from
19 equations (6), (7) and (8), namely that all the curves G1, G2 and
20 G3 converge at a single intercept point (I), at which $\Delta R/R$
21 equals 0, and $|\Delta\chi|^2$ equals approximately 0.5, regardless of the
22 measurement temperatures and material compositions of the layers.

23
24 As previously stated, the need for optimizing the roughness of
25 the interface for maximizing $\Delta R/R$ for any particular interface
26 is important. Accordingly, different preparation conditions,
27 such as different substrate temperatures, different deposition
28 rates and different sputtering pressure, will result in different
29 degrees of interfacial roughness. Accordingly, an optimal
30 interfacial surface roughness should be selected to maximize the

1 slopes of any curve G1, G2 or G3 and thereby achieving a maximum
2 $\Delta R/R$ for any interface Δx of the FM and spacer layers.

3
4 Example 18

5 Fig. 5 shows the value of $\Delta R/R$ for a GMR structure at three
6 peaks as a function of the following NiCo alloy compositions for
7 the FM layer. On the first GMR peak curve G1 in Fig. 5, the
8 following points represent the stated compositions:

9
10 Point H1: 30Ni:70Co

11 Point J1: Co

12 Point L1: 50Ni:50Co

13 Point M1: 70Ni:30Co

14 Point N1: 80Ni:20Co

15 Point P1: 90Ni:10Co

16 Point Q1: Ni

17
18 Example 19

19 On the second GMR peak curve G2 in Fig. 5, points R1 and S1
20 correspond to the respective compositions of points J1, H1, and
21 M1 along the first peak curve G1. R1 is 50Ni:50Co; S1 is
22 70Ni:30Co; T1 is 80Ni:20Co; and U1 is Ni.

23
24 Example 20

25 On the third GMR peak curve G3 in Fig. 5, V1 is 30Ni:70Co; W1 is
26 50Ni:50Co; X1 is 70Ni:30Co; and Y1 is Ni.

27
28 All previous examples of the invention consisted of FM materials
29 and spacers that were all FCC structure, i.e., FCC Systems.
30 However, Fig. 6 illustrates that the linear relationship of
31 equation (3) for the GMR sensor 20 (Fig. 2) at a temperature of

5° K is maintained when a BCC Systems is observed. The linear relationship is represented by an exemplary curves R1 (Fig. 6).

Example 21

On the GMR peak curve R1 (Fig. 6), the exemplary compositions are expressed as X-Y, where element X represents the material for the FM layers, and element Y represents the material for the conductive spacers 22.

<u>Point</u>	<u>X</u>	<u>Y</u>
g1	Fe	Cr
i1	Co	Cu
j1	Co	Ag

Points i1 and j1 both have FM and conductive spacer materials with FCC crystal structures (i.e., an FCC System). The FM and spacer materials at point g1, however, have BCC structures (i.e., a BCC System), and the latter point is also predicted by the linear relationship of the invention. For example, curve R1 in Fig. 6 may be expressed by the following equation (9), and relates to the GMR first peak:

$$(9) \quad \Delta R/R \cong 330 - 660 |\Delta\chi|^2$$

The foregoing example 21 confirms that both FCC and BCC Systems exhibit the same or substantially similar behavior as predicted by equations (3) and (4). Additionally it is shown that an FCC FM layer should be matched with an FCC conductive spacer, and a BCC FM layer should be matched with a BCC conductive spacer for best results. For example, when this crystal structure matching is maintained, (i.e., FCC on FCC and BCC on BCC FM and spacers), the relationships of equations 3 and 4 are exhibited.

1
2 Point p on Fig. 6 represents the GMR structure Fe Cu. This
3 structure presents an almost perfect electronegativity match
4 (i.e., ($|\Delta\chi| \approx 0.01$) between the Fe and Cu layers). Nonetheless,
5 this structure does not provide a high $\Delta R/R$ since Fe is a BCC
6 structure, while Cu is a FCC structure. Accordingly, inferior
7 $\Delta R/R$ is obtained and equations 3 and 4 are not observed due to
8 additional potential barriers created by the crystal structure
9 mismatch (i.e., BCC/FCC).

10
11 Although the desirability of matching the crystal structure
12 (i.e., FCC FM layer on an FCC spacer, or a BCC FM layer on an BCC
13 spacer), has been described, the need to match such crystal
14 structures may be mitigated in some instances. For example, a
15 BCC element or alloy may be forced by epitaxial effects of an
16 underlying FCC metal or alloy to form an FCC structure for a few
17 monolayers (i.e., 0.5 to 7 monolayers (ML)). The reciprocal
18 situation (i.e., an FCC material on a BCC material), would
19 produce a similar epitaxial effect. Additionally, in FCC Systems
20 some face centered tetragonal structures, representing nearly FCC
21 systems, may be used to advantage as well.
22

23 Fig. 7 is a chart that illustrates various exemplary combinations
24 and compositions for the FM layers and spacers, some of which are
25 explained by the following examples. In general, the FM layers
26 may be selected from a group comprised of Fe, Co, Ni, and their
27 alloys and their substitutional alloys. In addition, the
28 conductive spacer layers may be selected from a group comprised
29 of Au, Cu, Ag, Rh, Pt, Pd and substitutional alloys thereof, and
30 other suitable elements or intermetallic compounds possessing

sufficiently low resistivities. The Heusler alloys shown in Fig. 7 will be discussed later.

Example 22

Fig. 8 shows two curves, SL1 and SL2, plotting the electrical resistivity in microhm-cm versus the atomic composition for the Cu Au alloy system. Curve SL1 illustrates the relationship for alloys that have been quenched and cold worked (i.e., in a disordered state). Curve SL2 illustrates the relationship for alloys that are annealed at 200°C for the purpose of achieving an ordered superlattice structure. Fig. 8 further shows that the electrical resistivities of the ordered alloy relative to the same composition of the disordered alloy may be reduced significantly by annealing the alloys having predetermined atomic compositions. In the Cu Au system shown in Fig. 8, two such predetermined atomic compositions appear, the first (CP1) at 25 atomic percent of Au, and the second (CP2) at 50 atomic percent of Au. These compositions, at which the electrical resistivities of the alloys exhibit a minimum, are a result of an ordered superlattice and will be referred to herein as Critical Points (CP). Additional description of superlattice structures may be found in C. Barrett, "Structure of Metals, Crystallographic Methods, Principles, and Data", 269-296 (1952 2d) which is incorporated herein by reference.

Example 23

Fig. 9 shows two curves SL3, SL4, plotting the electrical resistivity versus atomic composition for the Cu Pt alloy system. Curve SL3 illustrates the relationship for alloys that are quenched and cold worked (disordered state). Curve SL4 illustrates the relationship for alloys that are annealed at

300°C for achieving an ordered superlattice structure. Fig. 9 further shows that the specific electrical resistivities of the ordered superlattice may be reduced significantly by annealing the alloys at two critical points CP3 (25 atomic percent Pt), and CP4 (50 atomic percent Pt).

While points CP1 and CP2 (Fig. 8), and points CP3 and CP4 (Fig. 9) reflect the most useful compositions, other compositions defined by the hatched areas A1 (Fig. 8) and B1, B2 (Fig. 9) between the envelopes of the disordered alloys (SL1, SL3) and the envelopes of the ordered alloys (SL2, SL4) may also be useful in providing a broader electronegativity selection range, while at the same time producing a partially ordered superlattice that will have some benefit in extending the thermal stability of spin valve and GMR sensors using the ordered alloys.

For example, the two alloy series in examples 22 and 23 may be annealed at between 100°C to 300°C in thin film form for approximately 0.5 hour to 4 hours to form the superlattice or partially ordered superlattice at appropriate composition. The invention uses the superlattices processed at or near critical points CP or within any of the shaded regions in the Cu Au binary system or the Cu Pt binary system or other binary systems. The shaded regions define the composition range within which some degree of superlattice order will occur and which may be used advantageously. The most advantageous compositions from a resistivity point of view are a 25 and 50 atomic percent Cu for both the Cu Au and Cu Pt systems. These superlattice alloys and compositions can be utilized to match or minimize the electronegativity difference of 80Ni:20Fe, for example, more advantageously. The benefits are shown in the following examples.

1 Similar superlattice alloys in the Cu Pd system (Cu_3Pd or CuPd)
2 may be used to advantage as well.

3
4 Example 24

5 A superlattice spacer 22 (Fig. 2) will provide a large mean free
6 path for electrons in the spacer while simultaneously minimizing
7 the electronegativity difference $|\Delta\chi|$ between the FM layers and
8 the superlattice spacers 22. For example, the Cu Pt superlattice
9 alloy (Fig. 9) exhibits a resistivity of about $3.5 \mu\Omega\text{-cm}$, which
10 is similar to the resistivity of gold, and an average
11 electronegativity of approximately 2.07 eV.

12
13 In this example 80Ni:20Fe is used as an FM layer. The
14 electronegativity of 80Ni:20Fe is about 2.084 eV and the
15 electronegativity of the CuPt superlattice alloy CP4 is
16 approximately 2.07 eV, resulting in an absolute electronegativity
17 difference $|\Delta\chi|$ of about 0.014 eV. This excellent match will
18 significantly minimize the detrimental interfacial scattering
19 component in the spin valve sensor 10 (Fig. 1) and the GMR sensor
20 20 (Fig. 2), and results in maximizing sensor signal output
21 $\Delta R/R$. This example also exhibits improved corrosion resistance
22 and thermal stability. In addition, adverse electromigration
23 effects in the sensor are minimized.

24
25 Example 25

26 In this example, the Cu Au superlattice alloy CP2 of Example 22
27 (Fig. 8) is used as a spacer, while Co is used as an FM layer.
28 Since the electronegativity of Co is about 2.05 eV and the
29 electronegativity of the Cu Au superlattice alloy CP2 is
30 approximately 2.07 eV, thus resulting in an absolute

1 electronegativity difference $\Delta\chi$ of 0.02, which provides an
2 excellent electronegativity match.

3
4 Example 26

5 In this example, a Cu Au superlattice CP2 (Fig. 8) is used as a
6 spacer, while an Ni₃Fe superlattice composition forms the FM
7 layers. The average electronegativity of the Cu Au superlattice
8 CP2 is about 2.07, which has an absolute electronegativity
9 difference of about 0.01 with the Ni₃Fe superlattice.

10
11 In addition to increasing the sensor output signals (represented
12 by, for example $\Delta R/R$), the dual superlattice structure increases
13 the thermal stability as well as the chemical stability of the
14 sensors 10 and 20 (Fig. 1 and 2). Since the superlattice alloys
15 are greatly more corrosion resistant than copper and the
16 ferromagnet alloys, the sensors 10 and 20 using the superlattices
17 formed at or near CPs result in a structure of superior
18 electromigration characteristics as well.

19
20 As mentioned earlier, one method for processing the superlattice
21 alloys is to anneal them between 100°C to 300°C for 10 to 200
22 minutes. An alternative method is to deposit the superlattice
23 alloys by sputtering or evaporation, at a relatively low rate, on
24 a sufficiently heated substrate. This slow deposition process
25 could form the superlattice structure without the need for
26 further thermal annealing.

27
28 Another advantage for using superlattice structures is that such
29 structures have high critical temperatures above which they
30 become disordered. These critical temperatures can exceed 300°C
31 in bulk, that is well above the normal operating temperatures of

1 the sensors 10 and 20 and also exceed the processing temperatures
2 normally used in preparing the sensors or superimposed write
3 structures for some devices.

4
5 The materials that may be used for FM layers to achieve the
6 preceding objective of minimizing $\Delta\chi$ are from the group of alloys
7 constituting (1) Fe, Ni, Co, or any combination of these
8 elements, and (2) any of the following elements or combinations
9 thereof: Au, Cu, Cr, Mn, Ti, V, Pt, Pd, Ru, Ir, Sn, Ta, Nb, Rh,
10 N, C, Zr, Hf, Y, La, and rare earth elements, having either FCC
11 or BCC structures or in amorphous forms containing a combination
12 of the above elements. A more extensive list of χ values that may
13 be used to implement the invention is provided in Appendix A,
14 which is incorporated by reference. The values of χ in Appendix A
15 were calculated using the data and methods described previously
16 in reference to Tables I and II.

17
18 Example 27

19 An additional example of desirable alloys to implement the
20 invention is provided by the following group of quaternary FM
21 alloys having minimal magnetostriction:

22
23 $(48\text{Co}:29\text{Ni}:23\text{Fe})_{(1-y)}\text{Pd}_y$, and $(26\text{Co}:44\text{Ni}:30\text{Fe})_{(1-y)}\text{Pd}_y$

24
25 In the foregoing two alloys, y is an atomic fraction of Pd with a
26 value between 0.12 to 0.30. These alloys display near zero
27 magnetostriction and low coercivity.

28
29 Also, the following alloys have near zero magnetostriction and
30 have χ values of 2.13. Each alloy can be matched with the

1 superlattice conductive spacer of CuPt whose χ is approximately
2 2.12:

3
4 33.6Co:20.3Ni:16.1Fe:30Pd, and
5 18.2Co:30.8Ni:21Fe:30Pd.
6

7 All previous examples were directed to randomly oriented crystals
8 of ferromagnets and conductive spacers. Because various crystal
9 faces are equally presented to a growing surface during the
10 fabrication of spin valve or GMR sensors, the electronegativity
11 of a randomly oriented crystallographic surface is expressed by
12 equation (10) wherein χ of each of the principal crystal faces
13 (i.e., $\langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 110 \rangle$), contributes equally to the
14 randomly oriented value of χ , as expressed by the following
15 equation:
16
17
18

19 (10) $\chi(\text{randomly oriented}) = 1/3 (\chi_{111} + \chi_{100} + \chi_{110})$
20

21 Fig. 10 illustrates the use of randomly oriented crystals in the
22 spin valve sensor 10 of Fig. 1. In this example, the crystalline
23 orientation of the substrate is random, and therefore the three
24 crystallographic orientations (i.e., $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$), have
25 approximately the same frequency of surface occupancy on the
26 substrate. As a result, the FM layer that is formed on top of the
27 substrate will develop the same random orientation as the
28 substrate by epitaxy. It is an object of the present invention to
29 match the average electronegativity of each layer to the average
30 electronegativity of the adjacent layers.
31

The following example 28 illustrates the effect of the mismatch of the electronegativity $|\Delta\chi|$ on the various crystal faces $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ of Ni and Cu.

Example 28

The electronegativity values and the electronegativity difference for the three faces of Cu and Ni are listed in the following table (data from Michaelson):

<u>Spacer Layer</u>			<u>FM Layer</u>		
<u>Cu (face)</u>	<u>χ_{Cu} (face)</u>		<u>Ni (face)</u>	<u>χ_{Ni} (face)</u>	<u>$\Delta\chi ^{1/2}$ (face)</u>
Cu(111)	2.041		Ni (111)	2.204	0.404
Cu(100)	1.87		Ni(100)	2.146	0.525
Cu(110)	1.821		Ni(110)	2.068	0.498

Applying equation (5) above, we can illustrate the impact on $\Delta R/R$ as a function of the face, assuming random crystal orientation for a spin value having Ni FM layers and a Cu spacer layer:

$$\Delta R/R = \frac{1}{3} \{ [32.30 - 64.60(0.404)]_{111} + [32.30 - 64.60(0.525)]_{100} + [32.30 - 64.60(0.498)]_{110} \}$$

In this equation, if $|\Delta\chi|^{1/2}$ is equal or greater than 0.5 then $\Delta R/R$ is set equal to zero (see Fig. 3), and thus:

$$\Delta R/R = \frac{1}{3} (6.21 + 0 + 0.19)\% \cong 2.13\%$$

This value approximates the experimentally observed value of 2.5 percent provided in example 11, thus indicating that there is a

1 probable weak preferred orientation in the sample, and it was not
2 completely random. This example illustrates that essentially one
3 crystal plane, in this case $\langle 111 \rangle$ plane, contributes over
4 approximately 90 percent of the $\Delta R/R$ observed value.

5
6 Thus, it is an aspect of this invention to select FM and spacer
7 layers having a single crystallographic orientation that will
8 maximize $\Delta R/R$, e.g. Ni FM layers and Cu spacer layers each
9 having $\langle 111 \rangle$ crystal orientations, and achieve significant
10 improvement in spin value sensor performance. The same aspect
11 applies to GMR structures.

12
13 In the above example, it was demonstrated in the Ni-Cu multilayer
14 system that approximately 90 percent of $\Delta R/R$ was due to crystals
15 in the spin valve layers having a $\langle 111 \rangle$ crystallographic
16 orientation. It is well known that even in films with random
17 surface orientations of $\langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 110 \rangle$ planes, epitaxy of
18 the succeeding Cu and FM films will occur, i.e., the orientation
19 effect is carried throughout the structure of the deposited
20 layer.

21
22 The electronegativity matching between adjacent layers, as
23 described in the foregoing equations may be implemented either
24 with polycrystalline FM layers and spacers having preferred
25 crystallographic orientations or single crystal FM layers and
26 spacers having preferred orientations. Fig. 11 illustrates the
27 use of polycrystalline FM layers and spacers having a preferred
28 orientation in the spin valve sensor 10 of Fig. 1. In this
29 example the surface crystalline orientation of the substrate has
30 been selected to be $\langle 111 \rangle$. As a result, the subsequent crystal
31 FM layer and spacers that are formed will develop the same $\langle 111 \rangle$

1 surface orientation. It is an object of the present invention to
2 match the electronegativities of the selected crystalline
3 orientation, which in this example is $\langle 111 \rangle$, of the juxtaposed
4 layers, rather than to match the average electronegativities of
5 these layers.

6
7 According to a preferred embodiment, the spin valve sensor 10
8 (Fig. 1) is formed by selecting a desired spacer material and a
9 preferred one of its three main crystalline orientations, for
10 example $\langle 111 \rangle$. Subsequently, the FM layers are selected such
11 that the χ of their corresponding faces with a $\langle 111 \rangle$ crystalline
12 orientation matches or substantially approximates the χ of the
13 selected spacer crystalline face (i.e., $\langle 111 \rangle$). Similarly, the
14 $\langle 110 \rangle$ and $\langle 100 \rangle$ surface faces can be matched as well by selecting
15 the proper alloys.

16 17 EXAMPLE 29

18 The selection of a preferred crystal orientation (i.e., $\langle 111 \rangle$,
19 $\langle 100 \rangle$ or $\langle 110 \rangle$), can be accomplished by selecting a substrate
20 such as magnesium oxide with a surface orientation of either
21 $\langle 111 \rangle$, $\langle 100 \rangle$ or $\langle 110 \rangle$. By selecting a single orientation, for
22 example $\langle 111 \rangle$, of the substrate and subsequently selecting a
23 ferromagnet and conductive spacer whose $\Delta\chi$'s for the selected
24 crystal orientations are minimized, and subsequently depositing
25 alternating layers of FM and conductive spacers on such an
26 oriented substrate, the resulting $\Delta R/R$'s will be greater than FM
27 and spacer structures having randomly oriented crystals.

28
29 Prior to the deposition of alternating ferromagnets and spacers
30 with preferred crystallographic orientations, it would be
31 desirable to deposit a layer of Pt, Pd, Au or Cu of 10 Å to 50 Å

1 with subsequent annealing at approximately 250-400°C to establish
 2 an epitaxial-oriented metal film from which subsequent epitaxy of
 3 the selected alternating FM and spacer materials are then
 4 subsequently deposited, with epitaxial integrity maintained at
 5 each subsequent layer in the formation of a spin valve or GMR
 6 structure.

7
 8 Since interfacial diffusion kinetics between the FM and the
 9 conductor spacer are expected to be a function of selected
 10 crystal orientation (i.e., $\langle 111 \rangle$, $\langle 100 \rangle$ or $\langle 110 \rangle$), the surface
 11 roughness of each selected orientation is optimized by optimizing
 12 the deposition conditions for each orientation. In this way, a
 13 maximum $\Delta R/R$ can be achieved for each principal orientation
 14 (i.e., $\langle 111 \rangle$, $\langle 100 \rangle$ or $\langle 110 \rangle$).

15
 16 Since no χ or ϕ values are found in the literature for alloys, χ
 17 values for the $\langle 111 \rangle$, $\langle 100 \rangle$, $\langle 110 \rangle$ faces must be estimated.
 18 First, equation (2) is used to calculate a χ for a randomly
 19 oriented alloy from the randomly oriented χ values of the
 20 constituent elements. Then, estimates are developed for
 21 correlation factors between χ values for randomly oriented FCC
 22 elements (χ_R) and χ values for FCC elements having a single
 23 orientation (χ_s). For example, using data from Michaelson and
 24 the relation $\chi_R = (\chi_{111} + \chi_{100} + \chi_{110})/3$, the following ratios were
 25 derived in FCC Systems:

$$\chi_{111} = 1.027 \chi_R$$

$$\chi_{100} = 1.007 \chi_R$$

$$\chi_{110} = 0.965 \chi_R$$

1
2 These ratios permit the estimation of χ_s of FM layers or spacers
3 having a single crystal orientation from the χ_R of FM layers or
4 spacers having a random crystal orientation, for the purpose of
5 minimizing $|\Delta\chi|$.

6
7 Although MR sensors have been reported wherein the FM layers and
8 spacers have been selected to have the same crystallographic
9 orientation, there has been no teaching of selecting an
10 orientation of an FM layer or spacer based on its χ to match a χ
11 of another preferred orientation of FM layer or spacer. Of the
12 reported MR sensors in which single crystallographic orientations
13 for FM layers and spacers were used, $|\Delta\chi|$ values were calculated
14 using the teachings of the inventor. The lowest $|\Delta\chi|$ thus
15 calculated was for a Co/Cu FCC System, wherein the $|\Delta\chi|$ was
16 approximately 0.14 eV.

17
18 An additional aspect of the invention is shown in Figs. 12 and
19 13, which illustrate a spin valve sensor 10A and a GMR sensor 20A
20 respectively comprised of compound FM layers. The spin valve
21 sensor 10A (Fig. 12) includes two or more compound FM layers
22 (FM1/FM2) and (FM3/FM4), each of which are composed of different
23 ferromagnetic materials. Similarly, the GMR sensor 20A (Fig. 13)
24 includes a plurality of electrically conductive spacers, such as
25 Spacer 1 and Spacer 2, that are interposed between and compound
26 FM layers, such as (FM1/FM2), (FM3/FM4), (FM4/FM5) and (FM6/FM7).
27 As explained in example 3 previously, the FM materials for these
28 compound layers should be selected so that the values of λ_s and
29 H_c for each material (e.g. FM1 and FM2) will combine to produce
30 low values of λ_s and H_c for the layers (e.g. FM1/FM2). Further,

1 the interfaces between the FM layers and spacers (e.g. FM2/Spacer
2 and FM3/Spacer) follow the electronegativity matching and other
3 selection criteria described herein.

4
5 In addition, the use of compound FM layers enables the adjustment
6 of the overall λ_s for the spin valve sensor 10A and the GMR
7 sensor 20A. For the structures of Fig. 12 (spin valve) and Fig.
8 13 (GMR), FM1 and FM4 may be identical compositions, or may be
9 different compositions, and the same applies to FM2 and FM3. It
10 may be advantageous, however, that FM2 and FM3 have the same
11 composition and that FM1 and FM4 have the same composition in
12 order to simplify processing because fewer sputtering targets
13 would be needed.

14
15 The basis for having two or more different compositions for FM1
16 and FM2 is that the magnetostriction thickness product of FM1 and
17 FM2 may be selected so that $\lambda_{FM1}t_{FM1}$ is approximately equal to -
18 $\lambda_{FM2}t_{FM2}$, where t is FM layer thickness, resulting in minimizing an
19 average λ_s for both layers, which average λ_s desirably approaches
20 zero for the compound FM interfaces. It is not necessary to
21 absolutely match the magnetostriction thicknesses products in
22 order to minimize magnetostriction. For example, if the ratio of
23 magnetostriction thickness products is even in the range of .3 to
24 3, the overall λ_s of the compound FM layer FM1/FM2 will be
25 reduced. Even an unbalanced thickness product of each layer will
26 lower λ_s , which minimizes λ_s of a compound FM layer structure.

27
28 As previously noted, the use of compound FM layer also enables
29 the minimization of the overall H_c of the layers because the H_c
30 of the layer is generally the average of the H_c values for each

1 FM material forming the layer (i.e., FM1 and FM2). For example,
2 an FM2 selected for a good χ match with the spacer may have a
3 high H_c . This adverse effect can be mitigated by selecting an
4 material for FM1 that has a very low H_c , without regard to
5 matching its χ with that of the spacer. Thus a low H_c for the
6 compound FM layers, such as less than 10 oersteds, may be
7 obtained.

8
9 It is important, however, that the χ of the FM layer adjacent to
10 the spacers (e.g., FM2 or FM3) be minimized relative to the χ of
11 the adjacent spacer. Similar conditions apply to the GMR
12 structure of Fig. 13 as well.

13
14 Thus, the compound FM structure in spin valve structures and GMR
15 structures, in combination with the preceding teaching requiring
16 the minimization of $\Delta\chi$ between FM and spacer, allows for
17 maximizing $\Delta R/R$ while simultaneously maximizing corrosion
18 resistance and minimizing the λ_s and H_c of compound ferromagnet
19 structures of spin valve structures or GMR structures or GMR
20 structures.

21 22 EXAMPLE 30

23 Heusler alloys represent another class of ferromagnetic materials
24 possessing a superlattice structure that may be partially or
25 fully ordered. Full ordering is possible at or very near to the
26 general stoichiometric composition M_2MnM_1 and may contain
27 ferromagnetic elements Co and Ni as well as the nonferromagnetic
28 elements Cu, Ir, Pd, Pt and Au for M_2 . M_1 may be Al, Ga, Ge, As,
29 In, Si, Sn or Bi. The Heusler alloys containing only Pt, Au, Pd
30 or Ir for M_2 (i.e., M_2 having a full complement of such element,

e.g., Au₂), exhibit Curie temperatures below room temperatures (i.e., below 300°K). Accordingly such alloys may, if they are not ferromagnetic and their bulk resistivity is less than approximately 30 $\mu\Omega$ -cm, be used as spacers for other ferromagnetic Heusler alloys. It is also possible to combine the following elements in M₂: Cu, Co, Ni, Pd, Pt, Au and Ir, for the purpose of fine control of the electronegativity of the Heusler alloy to minimize $\Delta\chi$ of the Heusler alloy and its spacer element or alloy or compound.

A representative series of FM Heusler alloys and their electronegativities is illustrated below:

<u>Heusler Alloy</u>	<u>χ Alloy</u>
Cu ₂ MnAl	1.80
Ni ₂ MnSn	1.93
Co ₂ MnGe	1.94
Co ₂ MnSi	1.93
Co ₂ MnSn	1.89
CuPdMnSn	1.92
NiAuMnSn	1.95

The FM Heusler alloys may be used in conjunction with spacer materials such as Cu, CuAu alloys (with Au of 5 to 15 atomic percent) and intermetallic spacers Al₂Au (with χ equal to 1.88) and PtAl₂ (with χ equal to 1.92). AgAu alloys may be used as well with Au less than 25 atomic percent.

By virtue of this invention, a method and means are provided for selecting the materials for spin valve and GMR sensors which simultaneously may have higher magnetoresistance output, improved corrosion resistance, improved coercivity, improved thermal

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